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(54) Title: DIVALENT CATION-CONTAINING WELL DRILLING AND SERVICING FLUIDS

(57) Abstract: The invention provides clay free, preferably biopolymer free, well drilling and servicing fluids comprising an aqueous divalent cation-containing water soluble salt, a bridging agent, and a pre-gelatinized crosslinked amylopectin starch suspending agent and fluid loss control additive. The concentration of the starch derivative is sufficient to provide the fluid with the following characteristics: (a) a low shear rate viscosity less than about 10,000 centipoise; (b) a high shear rate viscosity at 511 sec⁻¹ in the range from about 15 to about 70 centipoise measured at 120 °F; (c) a fluid loss less than about 10 milliliters as measured at 185 °F and 250 psi differential pressure across a 5 micron disk for 30 minutes; and (d) anti-settling characteristics as exhibited upon static aging the fluid for 16 hours at 185 °F. The low shear rate viscosity of the fluids can be increased without increasing the high shear rate viscosity above about 70 centipoise by incorporating magnesium oxide and/or dipotassium hydrogen phosphate in the fluids. The invention also provides a method of making the clay-free well drilling and servicing fluid and a process of drilling, completing, and working over a well with the clay-free fluid.

Divalent Cation-Containing Well Drilling and Servicing FluidsBackground of the Invention

The present invention relates to clay-free aqueous well drilling and servicing fluids, methods of preparation thereof, and method of drilling a well
5 therewith.

The use of fluids for conducting various operations in the boreholes of subterranean oil and gas wells which contact a producing formation are well known. Thus drill-in fluids are utilized when initially drilling into producing formations. Completion fluids are utilized when conducting various completion
10 operations in the producing formations. Workover fluids are utilized when conducting workover operations of previously completed wells.

One of the most important functions of these fluids is to seal off the face of the wellbore so that the fluid is not lost to the formation. Ideally this is accomplished by depositing a filter cake of the solids in the fluid over the surface of the borehole
15 without any loss of solids to the formation. In other words, the solids in the fluid bridge over the formation pores rather than permanently plugging the pores. This is particularly critical in conducting horizontal drilling operations within hydrocarbon-containing formations.

Many clay-free fluids have been proposed for contacting the producing zone of
20 oil and gas wells. See for example the following U.S. Patents: Jackson et al. 3,785,438; Alexander 3,872,018; Fischer et al. 3,882,029; Walker 3,956,141; Smithey 3,986,964; Jackson et al. 4,003,838; Mondshine 4,175,042; Mondshine

4,186,803; Mondshine 4,369,843; Mondshine 4,620,596; Dobson, Jr. et al. 4,822,500, and Johnson 5,504,062.

These fluids generally contain polymeric viscosifiers such as certain polysaccharides or polysaccharide derivatives, polymeric fluid loss control additives such as lignosulfonates, polysaccharides or polysaccharide derivatives, and bridging solids. As disclosed in Dobson, Jr. et al. U.S. Patent No. 4,822,500, a xanthan biopolymer and an epichlorohydrin crosslinked hydroxypropyl starch fluid loss control additive synergistically interact to provide suspension and fluid loss control in certain of these fluids.

10 Magnesium oxide has been disclosed for use in various polysaccharide-containing fluids to increase the thermal stability thereof. See for example the following U.S. patents: Jackson 3,852,201; Jackson 3,953,335; Hartfield 3,988,246; Jackson 4,025,443; and Dobson, Jr. 5,514,644.

It is well known that certain biopolymer-containing fluids are shear thinning, exhibiting a high low shear rate viscosity and a low high shear rate viscosity. A near zero shear rate (0.06 to 0.11 sec^{-1}) viscosity provides a numerical value related to the ability of a fluid to suspend particles or cuttings under static conditions. Conversely, viscosity measured at shear rates above 20 sec^{-1} relates to the hole cleaning capability of a fluid under annular flow conditions.

20 It is known to use dense brines as the base aqueous liquid for high density drilling and well servicing fluids. Such fluids contain minimal soluble bridging solids concentration and viscosifying polymer additives. The most commercially

available dense brines contain calcium chloride, calcium bromide, and zinc bromide. However, utilization of the brines has been limited. Generally, water-soluble polymers used for viscosity and filtration control do not perform well in calcium bromide and zinc bromide brines. Examples of the use of dense brines for use in well drilling and servicing fluids are as follows: Swartwout et al. U.S. Patent No. 5,612,293; Dobson, Jr. et al. U.S. Patent No. 5,616,541; Dobson, Jr. et al. U.S. Patent No. 5,728,652; Dobson, Jr. et al. U.S. Patent No. 5,728,654; Vollmer et al. U.S. Patent No. 5,785,747; and Dobson, Jr. et al. U.S. Patent No. 5,804,535.

Clean-up of the filter cake deposited on the sides of the borehole is a critical part of the completion process to ensure maximum productivity from a wellbore. Poor wall cake development allows particulates or liquids to enter the formation resulting in internal formation damage. Solids or polymers which have not been removed from the surface of a borehole can also impede the flow of hydrocarbons by plugging a prepacked screen during production. Filter cake removal is generally undertaken by treating the wellbore with concentrated acid solution, particularly hydrochloric acid. Dobson, Jr. et al. U.S. Patent No. 5,607,905 discloses the incorporation of certain inorganic peroxides into the filter cake which enhance the removal of the filter cake upon contacting it with an acidic solution. Brannon et al. U.S. Patent No. 5,881,813 discloses an enzyme-containing clean-up fluid for degrading the residual polymeric viscosifiers present in filter cakes from drill-in fluids or present in the formation from other well treating fluids.

While these improvements in formulating well drilling and servicing fluids from high density brines have had commercial success, there is still a need for such fluids which exhibit enhanced particulate suspension characteristics at lower viscosities and which are easier and more completely removed from wellbores, screens, and the like present in hydrocarbon-containing formations.

Summary of the Invention

The invention provides clay-free well drilling and servicing fluids comprising an aqueous brine which contains at least 1.2 equivalents per liter of a water soluble divalent cation salt, a particulate bridging agent which is insoluble in the aqueous brine, and a starch derivative which functions as a combination suspending agent and fluid loss control agent. The starch derivative is used in a concentration sufficient to provide the fluid with the following characteristics: (a) a low shear rate viscosity less than about 10,000 centipoise; (b) a high shear rate viscosity at 511 sec⁻¹ in the range from about 15 to about 70 centipoise measured at 120°F; (c) a fluid loss less than about 10 milliliters as measured at 185°F and 250 psi differential pressure across a 5 micron disk for 30 minutes; and (d) anti-settling characteristics as exhibited upon static aging the fluid for 16 hours at 185°F. The invention further provides that the low shear rate viscosity can be increased without raising the high shear rate viscosity above about 70 centipoise by incorporating magnesium oxide and/or dipotassium hydrogen phosphate in the fluids.

The preferred modified starch comprises amylopectin, such as a waxy starch, that has been crosslinked to the extent that the viscosity of a basic aqueous amylopectin starch suspension undergoing crosslinking is within about 25% to about 60% of the maximum viscosity that can be obtained, preferably from about
5 25% to less than about 50%, and pre-gelatinized.

The invention further comprises a process for preparing the clay-free fluids, and a process of drilling, completing, or working over a well with the clay-free fluids.

While the invention is susceptible to various modifications and alternative
10 forms, specific embodiments thereof will hereinafter be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the invention is to cover all modifications and alternatives falling within the spirit and scope of the invention as expressed in the appended claims.

15 The compositions can comprise, consist essentially of, or consist of the stated materials. The method can comprise, consist essentially of, or consist of the stated steps with the stated materials.

Detailed Description of the Invention

The present invention is based on the discovery that certain starch derivatives
20 function in certain dense brines to impart suspension characteristics and fluid loss control characteristics to the brines.

The brines useful in the compositions and processes of the invention contain at least 0.6 equivalents per liter of one or more water soluble divalent cation salts. Preferred divalent cations are the alkaline earth metal salts and/or zinc salts. The preferred anion is a halide, most preferably chloride and/or bromide. Most preferred divalent cations are selected from the group consisting of calcium, magnesium, zinc, and mixtures thereof. Thus the most preferred salts are selected from the group consisting of calcium chloride, calcium bromide, magnesium chloride, magnesium bromide, zinc chloride, zinc bromide and mixtures thereof. Other divalent cation water soluble salts may be present in the brine.

10 The preferred brines have a density of at least about 10.0 ppg.

Starch is a natural polymer containing an abundance of hydroxyl groups. Each anhydroglucose unit contains two secondary hydroxyls and a large majority contain primary hydroxyls. These hydroxyls potentially are able to react with any chemical capable of reacting with alcoholic hydroxyls. This would include a wide range of compounds such as acid anhydrides, organic chloro compounds, aldehydes, epoxy, ethylenic compounds, etc. When the specified chemical contains two or more moieties capable of reacting with hydroxyl groups, there is the possibility of reacting two different hydroxyls resulting in crosslinking between hydroxyls on the same molecule or on different molecules.

20 The chemistry of starch and the preparation of a multitude of derivatives thereof is well known. A book entitled "Modified Starches: Properties and Uses," by O.B. Wurzburg, 1986 (CRC Press, Inc., Boca Raton, Florida, U.S.A.) is an

excellent source for information in the preparation of modified starches. In regards to the preparation of the crosslinked starches of this invention, the chapter entitled "Crosslinked Starches" is particularly pertinent.

Representative crosslinking materials are epichlorohydrin and other
5 epihalohydrins, formaldehyde, phosphorous oxychloride, trimetaphosphate, dialdehydes, vinyl sulfone, diepoxides, diisocyanates, bis(hydroxymethyl) ethylene urea, and the like. The preferred crosslinking compound is epichlorohydrin.

Crosslinking of the starch results in an increase in the molecular weight of the starch and an increase in the viscosity of aqueous dispersions of the starch.

10 The reaction conditions used in making crosslinked starches vary widely depending upon the specific bi-or polyfunctional reagent used for the crosslinking. In general, most of the reactions are run on aqueous suspensions of starch at temperatures ranging from room temperature up to about 50°C. Often an alkali such as sodium hydroxide is used to promote reaction. The reactions are normally
15 run under neutral to fairly alkaline conditions, but below the level which will peptize or swell the starch. If the crosslinking reaction is run in an aqueous suspension of starch, when the desired level of crosslinking (usually as measured by some type of viscosity or rheology test) is reached, the starch suspension is neutralized and the starch is filtered and washed to remove salts, any unreacted
20 reagent, and other impurities produced by side reactions of the crosslinking reagent with water. Konigsberg U.S. Pat. No. 2,500,950 discloses the crosslinking of starch with epoxyhalogen compounds such as epichlorohydrin. If desired, the

starch can be suspended in non-aqueous liquids or aqueous solutions containing water soluble organic liquids during crosslinking. See for example Kesler et al. U.S. Patent No. 2,845,417, incorporated herein by reference.

It is preferred that the amylopectin starch for use in the present invention be crosslinked with epichlorohydrin in a basic aqueous starch suspension at a temperature and for a period of time such that the Brabander viscosity of the suspension is within about 25% to about 60% of the maximum attainable viscosity, preferably from about 25% to less than about 50% of the maximum attainable viscosity. The viscosity will vary by the amount of crosslinking and the test conditions, i.e., temperature, concentrations, etc. A viscosity peak indicates maximum crosslinking. When the desired viscosity is reached, the crosslinking reaction is terminated. A Brabender Viscometer is a standard viscometer readily available on the open market and well known to those skilled in the art.

As indicated, the crosslinked amylopectin starch of this invention is pre-gelatinized. The term "gelatinization" is well known in the art and is generally used to describe the swelling and hydration of starches. Starch granules are insoluble in cold water but imbibe water reversibly and swell slightly. However, in hot water, a large irreversible swelling occurs producing gelatinization. Gelatinization takes place over a discrete temperature range that depends on starch type. Since gelatinization increases the viscosity of a starch suspension, the gelatinization of the starch is preferably conducted after the amylopectin starch is crosslinked to the desired extent as indicated herein. Certain chemicals increase

the gelatinization temperature range of starches and thus such chemicals can be present during the crosslinking of the amylopectin in order that the crosslinking temperature can be increased without gelatinization of the starch occurring. The term "pre-gelatinized" indicates that the crosslinked amylopectin has been
5 gelatinized such that the crosslinked amylopectin does not undergo gelatinization upon adding it to the brines of the present invention.

The crosslinked amylopectin is normally gelatinized by heating the crosslinked amylopectin at a temperature above the gelatinization temperature, such as during drying of the crosslinked starch slurry.

10 As indicated, the pre-gelatinized crosslinked amylopectin for use in the present invention is preferably derived from a waxy starch, preferably waxy corn (maize) starch. As is known, waxy starches are virtually all amylopectin whereas common starches contain both amylose and amylopectin molecules. For the purposes of disclosing and claiming this invention, the amylopectin contains less than about
15 10% by weight amylose, preferably not more than about 5% amylose and most preferably less than 1% amylose.

The brines may contain other compatible water soluble salts therein. The term "compatible" as used herein in regards to the present invention refers to a salt which does not result in precipitate formation in the brine and/or which does not
20 prevent the disclosed pre-gelatinized crosslinked amylopectin starch from providing the brines with the characteristics set forth herein.

The fluids of this invention may contain other functional additives to impart specific properties to the fluids. Thus the fluids may contain weight materials (which may function as bridging agents in an appropriate particle size range), corrosion inhibitors, anti-oxidants, oxygen scavengers, reducing agents, supplemental fluid loss control additives, supplemental viscosifiers, and the like.

The fluids of this invention must have a bridging agent incorporated therein. The bridging agents useful in this invention are well known in the art. They are solid, particulate, water soluble salts or acid soluble materials the particles of which have been sized to have a particle size distribution sufficient to seal off the pores of the formations contacted by the well drilling and servicing fluid as is well known in the art. See for example Dobson, Jr. et al U.S. Patent No. 5,616,541 and Johnson U.S. Patent No. 5,504,062, both incorporated herein by reference. The bridging agent must not be appreciably soluble in the liquid used to prepare the fluid.

Representative water soluble salt bridging agents include sodium chloride, potassium chloride, magnesium chloride, potassium formate, calcium bromide, calcium chloride, and the like.

Preferred bridging agents have a specific gravity less than about 3.0 and are sufficiently acid soluble such that they readily decompose upon acidizing the filter cake and deposits in the borehole. Representative bridging agents are calcium carbonate, dolomite (calcium magnesium carbonate), colemanite, ulexite, analcite, apatite, bauxite, brucite, gibbsite, and hydrotalcite.

The concentration of the bridging agents will be sufficient that, together with the concentration of the starch derivative, the fluids exhibit a fluid loss less than about 10 milliliters as measured at 185°F and 250 psi differential pressure across a 5 micron disk for 30 minutes. Generally the concentration of the bridging agents
5 will be from about 5 ppb to about 50 ppb, preferably from about 10 ppb to about 30 ppb.

The concentration of the starch derivative must be sufficient to provide the fluid with the following characteristics: (a) a low shear rate viscosity less than about 10,000 centipoise; (b) a high shear rate viscosity at 511 sec⁻¹ in the range
10 from about 15 to about 70 centipoise measured at 120°F; (c) a fluid loss less than about 10 milliliters as measured at 185°F and 250 psi differential pressure across a 5 micron disc for 30 minutes; and (d) anti-settling characteristics as exhibited upon static aging the fluid for 16 hours at 185°F. Generally, the concentration of the starch derivative will be from about 5 ppb to about 12 ppb, preferably from about 6
15 ppb to about 11 ppb, and most preferably from about 7 ppb to about 10 ppb.

It is a novel feature of the invention that the starch derivative imparts excellent suspension characteristics to the fluids at the low viscosities imparted to the fluids. This is in direct contrast with fluids containing water soluble polymer viscosifiers, such as biopolymers, such as xanthan gum, scleroglucan gum, succinoglycan gum,
20 and the like, in the dense brines used in the fluids of this invention.

It is preferred that the fluids of the invention do not contain any polymeric viscosifiers, such as biopolymers, i.e., the preferred fluids are biopolymer free.

Without being limited thereby, we believe that the buoyancy of the brines contributes to the suspension characteristics of the brines. Thus as the density of the dense brines increases, less viscosity development by the starch derivative is necessary for the excellent suspension characteristics observed. This has not been
5 previously known. Indeed, prior art fluids as exemplified by the patents disclosed hereinbefore indicate that the fluids contain a biopolymer or amorphous silica viscosifier and suspending agent and generally a starch or derivative thereof as a filtration control additive.

The fluids of the invention may be prepared and the method of the invention
10 practiced, by mixing the dense divalent cation-containing brine as set forth herein with the starch derivative, and the bridging agent, and any optional additives as disclosed herein. The concentration of the starch as disclosed herein is that concentration which will provide the fluid with the following characteristics: (a) a low shear rate viscosity less than about 10,000 centipoise; (b) a high shear rate
15 viscosity at 511 sec^{-1} in the range from about 15 to about 70 centipoise measured at 120°F ; (c) a fluid loss less than about 10 milliliters as measured at 185°F and 250 psi differential pressure across a 5 micron disk for 30 minutes; and (d) anti-settling characteristics as exhibited upon static aging the fluid for 16 hours at 185°F .

After static aging the fluids in sealed pint jars, any separation or syneresis was
20 noted by measuring the depth of separation. For purposes of this invention, the fluids of the invention exhibit no more than $\frac{1}{4}$ inch separation which is about 10% by volume. The settling characteristics of the aged fluids is then determined by

inserting a spatula carefully into the fluids and observing if any solids had separated from the fluid. For purposes of this invention, the fluids exhibit no settling of solids.

The fluids of the invention are useful in various petroleum recovery operations such as well drilling, including drilling into hydrocarbon-containing formations, completion, workover and the like all as are well known in the art. Specifically the fluids of the invention are useful in drilling a well wherein the drilling fluid is circulated within a borehole being drilled as drilling proceeds, and in well completion and workover methods wherein a subterranean formation is contacted with an aqueous fluid to form a bridge and seal on the formation, all as are well known in the art.

The low shear rate viscosity (LSRV) for purposes of this invention is obtained using a Brookfield Model LVTDV-1 viscometer having a number 1 or 2 spindle at 0.3 revolutions per minute (shear rate of 0.0636 sec^{-1}). The fluid loss characteristics of the fluids are obtained by a modified API filtration test. Thus to an API high temperature filtration cell with removable end cages is added a 5 micron disk (i.e., an aluminum oxide (Aloxite™) ceramic disk having 5 micron pore throats, from 600 to 750 md permeability, which is 2.5 inches in diameter and 0.25 inch in depth) saturated with water. The fluid to be tested is poured along the inside edge of the filtration cell. The filtration test is then conducted for 30 minutes at the desired temperature of 185°F under a pressure differential of 250 pounds per square inch supplied by nitrogen. The spurt loss is measured as the amount of fluid

expelled from the filtration cell until the flow of fluid is reduced to drops. The fluid loss is measured as the total amount of fluid collected in 30 minutes.

The viscosities in centipoise at 1022 sec^{-1} , 511 sec^{-1} , 340.7 sec^{-1} , 170.3 sec^{-1} , 10.22 sec^{-1} , and 5.11 sec^{-1} are obtained by utilizing a Fann 35 Viscometer at 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm by multiplying the Fann dial reading by 0.5, 1, 1.67, 3, 50, and 100, respectively.

In order to more completely describe the invention, the following non-limiting examples are given. In these examples and this specification, the following abbreviations may be used: API = American Petroleum Institute; XLAPS = the pre-gelatinized epichlorohydrin crosslinked amylopectin starch derivative of this invention which has been crosslinked to the extent that the viscosity of a basic aqueous amylopectin starch suspension undergoing crosslinking is within about 25% about 60% of the maximum viscosity which can be obtained; LSRV = Brookfield low shear rate viscosity at .03 revolutions per minute; 0.0636 sec^{-1} , in centipoise; high shear rate viscosity = Fann viscosity at 511 sec^{-1} in centipoise; sec = second(s); ppg = pounds per gallon; ppb = pounds per 42 gallon barrel; °F = degrees Fahrenheit; ml = milliliters; min = minutes; cp = centipoise; rpm = revolutions per minute; in = inches.

Example 1

12.5 ppg fluids were prepared containing 0.98 bbl equivalents of a 12.25 ppg CaBr₂ brine, 23 ppb of a calcium carbonate bridging agent, and the concentrations of XLAPS, xanthan gum, scleroglucan gum, and succinoglycan gum set forth in

Table 1. The rheology of the fluids before and after aging 16 hours at 85°C (185°F), and an indication of the suspension characteristics of the fluids after the static aging, were measured.

The data are set forth in Table 1.

Example 2

13.5 ppb fluids were prepared containing 0.81 bbl equivalents of a 14.2 ppb CaBr_2 brine, 0.16 bbl equivalents of water, 26 ppb calcium carbonate bridging agent, and the concentrations of XIAPS, xanthan gum, scleroglucan gum, and succinoglycan gum set forth in Table 2. The fluids were evaluated as in Example 1. The data are set forth in Table 2.

Example 3

14.5 ppb fluids were prepared containing 0.74 bbl equivalents of a 14.2 ppb CaBr_2 brine, 0.14 bbl equivalents of a 19.2 ppb $\text{CaBr}_2/\text{ZnBr}_2$ brine, 0.10 bbl equivalents of water, 0.25 ppb magnesium oxide, 23 ppb calcium carbonate bridging agent, and the concentrations of XLAPS, xanthan gum, scleroglucan gum, and succinoglycan gum set forth in Table 3. The fluids were evaluated as in Example 1. The data are set forth in Table 3.

Example 4

15.5 ppb fluids were prepared containing 0.58 bbl equivalents of a 14.2 ppb
20 CaBr₂ brine, 0.31 bbl equivalents of a 19.2 ppb CaBr₂/ZnBr₂ brine, 0.08 bbl
equivalents of water, 0.25 ppb magnesium oxide, 25 ppb calcium carbonate
bridging agent, and the concentrations of XLAPS, xanthan gum, scleroglucan gum,

and succinoglycan gum set forth in Table 4. The fluids were evaluated as in Example 1. The data are set forth in Table 4.

Example 5

16.5 ppg fluids were prepared containing 0.41 bbl equivalents of a 14.2 ppg
5 CaBr₂ brine, 0.52 bbl equivalents of a 19.2 ppg CaBr₂/ZnBr₂, 0.05 bbl equivalents of water, 0.25 ppb of magnesium oxide, 23 ppb calcium carbonate bridging agent, and the concentrations of XLAPS, xanthan gum, scleroglucan gum, and succinoglycan gum set forth in Table 5. The fluids were evaluated as in Example 1. The data are set forth in Table 5.

10 In Tables 1-5, fluids C, D and E which don't contain the XLAPS of this invention are not examples of the invention, and are presented for comparison purposes only. The data indicate the excellent suspension characteristics of the fluids containing the XLAPS even at very low LSRV, and the very poor suspension characteristics of the fluids containing only the biopolymers.
15 Incorporation of a biopolymer into the XLAPS-containing fluids increased the high shear rate viscosity and affected the LSRV in various ways depending upon the density of the fluids. The data also indicate that, in general, the LSRV decreases and the high shear rate viscosity increases as the concentration of zinc bromide in the fluids increases. However, the excellent suspension characteristics of the fluids
20 was maintained.

Example 6

CaCl₂ fluids having densities of 9.5, 10.35 and 11.3 ppg were prepared each containing 8 ppb XIAPS and the concentration of MgO and calcium carbonate bridging agent set forth in Table 6. The fluids were evaluated as in Example 1. The
5 data obtained are set forth in Table 6.

The data indicate that: (1) the density of the fluids should be greater than 9.5 ppg, preferably at least about 10.0 ppg; (2) magnesium oxide can be added to increase the viscosity of the fluids, as desired, especially the LSRV; and (3) the excellent suspension characteristics of the fluids of the invention even
10 at low LSRV.

Example 7

14.6 ppg CaBr₂/ZnBr₂ fluids were prepared each containing 8 ppb XIAPS, 24 ppb CaCO₃ bridging agent, 0.71 bbl 14.2 ppg CaBr₂, 0.11 bbl water, 0.17 bbl 19.2 ppg CaBr₂/ZnBr₂, and the concentrations of MgO, MgO₂, sodium thiosulfate, and
15 K₂HPO₄ set forth in Table 7. The fluids were evaluated as in Example 1. The data obtained are set forth in Table 7.

The data indicate that the magnesium oxide enhanced the thermal stability of the fluids containing the magnesium peroxide and sodium thiosulfate, and that the K₂HPO₄ increases the viscosity of the fluid after aging at 185°F, especially the
20 LSRV.

Example 8

A 14.6 ppb $\text{CaBr}_2/\text{ZnBr}_2$ fluid was prepared as in Example 7 containing 8 ppb XLAPS, 0.25 ppb MgO , and 24 ppb CaCO_3 bridging agent. The rheology of the fluid was measured at 120°F initially and after aging the fluid for the time set forth in Table 8 at 185°F. The data obtained are set forth in Table 8.

The data indicate the excellent thermal stability and suspension characteristics of the fluid.

Example 9

10.35 ppb MgCl_2 fluids were prepared containing 0.97 bbl of 10.0 ppb MgCl_2 brine, 8 ppb XLAPS, 26 ppb calcium carbonate bridging agent, and either 0 or 0.25 ppb MgO . The fluids were evaluated as before. The data obtained are set forth in Table 7.

The data indicate the excellent suspension characteristics of the XLAPS in MgCl_2 -containing brines, and the increase of the LSRV upon addition of the MgO .

Example 10

The high temperature, high pressure fluid loss for fluids 4-A, Table 4, and 5-A, Table 5, were determined at 185°F, 250 psi differential pressure across a 5 micron disk. The data obtained are as follows. Fluid 4-A: Initial – Spurt Loss = 1.5 ml, 30 min. = 3 ml; Aged @ 185°F – Spurt Loss = 2.5 ml, 30 min = 3.5 ml. Fluid 5-A: Initial – Spurt Loss = 1.5 ml, 30 min = 3 ml; Aged @ 185°F – Spurt Loss = 2 ml, 30 min = 4 ml.

These data illustrate the excellent fluid loss characteristics of the fluids of this invention.

The data in the Tables indicate that the LSRV of the fluids of this invention can be increased by the addition of magnesium oxide, dipotassium hydrogen phosphate, or biopolymers to the fluids, particularly after subjecting the fluids to elevated temperatures as would occur on using the fluids in the drilling or servicing of wells. The data also indicate that only low concentrations of the biopolymer can be incorporated into the fluids without unduly raising the high shear rate viscosity, i.e., at 511 sec^{-1} . Thus the LSRV of the fluids can be increased without unduly raising the high shear rate viscosity by the addition of magnesium oxide and/or dipotassium hydrogen phosphate to the fluids, preferably in an amount from about 0.1 ppb to about 5 ppb. It is another aspect of the invention to increase the low shear rate viscosity of the fluids of the invention without increasing the high shear rate viscosity above about 70 centipoise by the addition of magnesium oxide and/or dipotassium hydrogen phosphate to the fluids. Thus the low shear rate viscosity of the fluids can be greater than 10,000 centipoise upon the addition of an additive which raises the low shear rate viscosity of the fluids without raising the high shear rate viscosity above about 70.

Table 112.5 ppb CaBr₂ Fluids

<u>Fluid</u>	<u>1-A</u>	<u>1-B</u>	<u>1-C</u>	<u>1-D</u>	<u>1-E</u>	<u>1-F</u>	<u>1-G</u>	<u>1-H</u>
XLAPS, ppb	8.0	10.0	0	0	0	8.0	8.0	8.0
5 Xanthan, ppb	0	0	1.5	0	0	1.5	0	0
Scleroglucan, ppb	0	0	0	1.5	0	0	1.5	0
Succinoglycan, ppb	0	0	0	0	1.5	0	0	1.5

Initial Rheology at 120°F

1022 sec ⁻¹ , cp	18	30	15.5	14.5	11	80	49	65
10 511 sec ⁻¹ , cp	22	40	19	21	12	11	4	70
10.22 sec ⁻¹ , cp	150	150	50	350	0	650	850	300
0.0636 sec ⁻¹ , cp	3039	2600	1920	9,878	120	17,700	54,300	700
STI	138	65	101	470	10	155	776	8

Static Aged at 185°F for 16 hours

15 Separation	None	None	Total	None	Total	None	None	None
Settling	None	None		None		None	None	None
1022 sec ⁻¹ , cp	17.5	29.5	14.5	14	10	75	47.5	55
511 sec ⁻¹ , cp	20	38	17	21	11	105	72	72
10.22 sec ⁻¹ , cp	50	150	50	350	100	500	900	150
20 0.0636 sec ⁻¹ , cp	440	500	600	12,357	0	10,300	50,700	900
STI	22	13	5	588	0	98	704	12.5

Table 213.5 ppg CaBr₂ Fluids

<u>Fluid</u>	<u>2-A</u>	<u>2-B</u>	<u>2-C</u>	<u>2-D</u>	<u>2-E</u>	<u>2-F</u>	<u>2-G</u>	<u>2-H</u>
XI.APS, ppb	7.0	10.0	0	0	0	8.0	8.0	8.0
5 Xanthan, ppb	0	0	1.5	0	0	1.5	0	0
Scleroglucan, ppb	0	0	0	1.5	0	0	1.5	0
Succinoglycan, ppb	0	0	0	1.5	0	0	1.5	

Initial Rheology at 120°F

1022 sec ⁻¹ , cp	18.5	35	23.5	4.5	4.5	89	37.5	65
10 511 sec ⁻¹ , cp	23	47	30	4	5	140	44	85
10.22 sec ⁻¹ , cp	200	200	150	0	0	900	100	150
0.0636 sec ⁻¹ , cp	5700	9200	280	60	100	13,500	300	800
STI	248	196	9	15	20	96	7	9

Static Aged at 185°F for 16 hours

15 Separation, in	None	None	Total	Total	Total	None	0.5	None
Settling	None	None				None	None	None
1022 sec ⁻¹ , cp	20.5	40	19.5	4	25.5	95	37.5	99
511 sec ⁻¹ , cp	25	53	24	4	33	145	43	142
10.22 sec ⁻¹ , cp	150	200	50	0	150	1100	150	1000
20 0.0636 sec ⁻¹ , cp	1180	7200	100	20	280	19,800	4800	16,100
STI	47	136	4	5	9	137	112	113

Table 3

14.5 ppg CaBr₂/ZnBr₂ Fluids

<u>Fluid</u>		<u>3-A</u>	<u>3-B</u>	<u>3-C</u>	<u>3-D</u>	<u>3-E</u>	<u>3-F</u>	<u>3-G</u>	<u>3-H</u>
	XLAPS, ppb	7.0	10.0	0	0	0	8.0	8.0	8.0
5	Xanthan, ppb	0	0	1.5	0	0	1.5	0	0
	Scleroglucan, ppb	0	0	0	1.5	0	0	1.5	0
	Succinoglycan, ppb	0	0	0	0	1.5	0	0	1.5
<u>Initial Rheology at 120°F</u>									
	1022 sec ⁻¹ , cp	19	38.5	14	13	3.5	75	72.5	31.5
10	511 sec ⁻¹ , cp	23	50	17	14	4	109	90	37
	10.22 sec ⁻¹ , cp	150	200	100	100	0	600	150	50
	0.0636 sec ⁻¹ , cp	2200	8000	20	60	60	6900	500	1300
	STI	96	160	1	4	15	63	6	35
<u>Static Aged at 185°F for 16 hours</u>									
15	Separation	None	None	Total	Total	Total	None	None	None
	Settling	None	None				None	None	None
	1022 sec ⁻¹ , cp	19.5	41	25	10	20.5	78.5	66	74
	511 sec ⁻¹ , cp	23	53	34	11	26	117	80	107
	10.22 sec ⁻¹ , cp	100	200	200	100	150	900	150	850
20	0.0636 sec ⁻¹ , cp	680	3800	200	20	140	18,700	600	10,600
	STI	30	72	6	2	5	160	7.5	99

Table 4

15.5 ppg CaBr₂/ZnBr₂ Fluids

<u>Fluid</u>	<u>4-A</u>	<u>4-B</u>	<u>4-C</u>	<u>4-D</u>	<u>4-E</u>	<u>4-F</u>	<u>4-G</u>	<u>4-H</u>
XIAPS, ppb	8.0	10.0	0	0	0	8.0	8.0	8.0
5 Xanthan, ppb	0	0	1.5	0	0	1.5	0	0
Scleroglucan, ppb	0	0	0	1.5	0	0	1.5	0
Succinoglycan, ppb	0	0	0	0	1.5	0	0	1.5

Initial Rheology at 120°F

1022 sec ⁻¹ , cp	29	46.5	11.5	16	5.5	96	89	36.5
10 511 sec ⁻¹ , cp	37	61	13	16	6	145	110	43
10.22 sec ⁻¹ , cp	150	300	0	0	50	1050	150	50
0.0636 sec ⁻¹ , cp	2000	7600	40	20	80	6800	600	400
STI	54	126	3	1	13	47	5	9

Static Aged at 185°F for 16 hours

15 Separation	None	None	Total	Total	Total	None	None	None
Settling	None	None				None	None	None
1022 sec ⁻¹ , cp	31.5	47	21.5	12	29.5	100	77	90
511 sec ⁻¹ , cp	39	61	27	12	39	148	85	126
10.22 sec ⁻¹ , cp	150	200	150	0	200	1000	150	900
20 0.0636 sec ⁻¹ , cp	900	2400	80	0	80	7800	300	7400
STI	23	39	3	0	2	53	4	59

Table 5

16.5 ppg CaBr₂/ZnBr₂ Fluids

<u>Fluid</u>	<u>5-A</u>	<u>5-B</u>	<u>5-C</u>	<u>5-D</u>	<u>5-E</u>	<u>5-F</u>	<u>5-G</u>	<u>5-H</u>
XLAPS, ppb	8.0	10.0	0	0	0	8.0	8.0	8.0
5 Xanthan, ppb	0	0	1.5	0	0	1.5	0	0
Scleroglucan, ppb	0	0	0	1.5	0	0	1.5	0
Succinoglycan, ppb	0	0	0	0	1.5	0	0	1.5
<u>Initial Rheology at 120°F</u>								
1022 sec ⁻¹ , cp	38	44.5	10.5	22	6	117	120	93.5
10 511 sec ⁻¹ , cp	42	55	12	24	7	165	150	112
10.22 sec ⁻¹ , cp	150	200	100	50	50	900	250	200
0.0636 sec ⁻¹ , cp	500	7800	40	0	20	4800	800	600
STI	12	142	3	0	3	29	5	5
<u>Static Aged at 185°F for 16 hours</u>								
15 Separation	None	None	Total	Total	Total	None	None	None
Settling	None	None				None	None	None
1022 sec ⁻¹ , cp	37.5	65	20	16.5	20.5	127	92	144
511 sec ⁻¹ , cp	46	83	25	18	25	178	108	198
10.22 sec ⁻¹ , cp	150	300	100	0	100	1050	200	1350
20 0.0636 sec ⁻¹ , cp	500	2100	360	20	200	5700	400	15,000
STI	11	25	14	1	8	228	4	76

Table 6
CaCl₂ Fluids
8 ppb XLAPS

	<u>Fluid</u>	<u>6-A</u>	<u>6-B</u>	<u>6-C</u>	<u>6-D</u>	<u>6-E</u>	<u>6-F</u>
5	Density, ppg	9.5	9.5	10.35	10.35	11.3	11.3
	9.15 ppg CaCl ₂ , bbl	0.97	0.97	0	0	0	0
	10.0 ppg CaCl ₂ , bbl	0	0	0.97	0.97	0	0
	11.0 ppg CaCl ₂ , bbl	0	0	0	0	0.97	0.97
	CaCO ₃ , ppb	25	25	26	26	25	25
10	MgO, ppb	0	0.25	0	0.25	0	0.25
<u>Initial Rheology at 120°F</u>							
	1022 sec ⁻¹ , cp	8.5	11.5	15	19	26.5	31
	511 sec ⁻¹ , cp	11	17	18	27	33	41
	10.22 sec ⁻¹ , cp	50	250	50	300	150	300
15	0.0636 sec ⁻¹ , cp	5520	15,737	2300	16,357	4000	20,296
	STI	502	926	128	606	121	495
<u>Static Aged at 185°F for 16 hours</u>							
	Separation, in	1	1.25	0.25	0.25	0.25	None
	Settling	Settling	Settling	None	None	None	None
20	1022 sec ⁻¹ , cp	8.5	13	15.5	22.5	26	35
	511 sec ⁻¹ , cp	11	19	19	33	33	48
	10.22 sec ⁻¹ , cp	50	250	0	480	150	500
	0.0636 sec ⁻¹ , cp	3500	21,695	1120	33,693	1820	33,896
	STI	318	1142	59	1021	55	706

25

Table 7

8 ppb XLAPS

		<u>14.6 ppb CaBr₂/ZnBr₂ Fluids</u>				<u>10.35 ppb MgCl₂</u>	
<u>Fluid</u>		<u>7-A</u>	<u>7-B</u>	<u>7-C</u>	<u>7-D</u>	<u>9-A</u>	<u>9-B</u>
5	MgO, ppb	0.25	0	0	0.25	0	0.25
	Mg Peroxide, ppb	0.5	0.5	0.5	0	0	0
	Sodium Thiosulphate, ppb	0.5	0.5	1.0	0	0	0
	K ₂ HPO ₄ , ppb	0	0	3.0	0	0	0
<u>Initial Rheology at 120°F</u>							
10	1022 sec ⁻¹ , cp	23.5	24	23	26.5	20.5	19
	511 sec ⁻¹ , cp	30	30	29	34	23	27
	1022 sec ⁻¹ , cp	200	100	100	200	150	50
	0.0636 sec ⁻¹ , cp	3200	3500	3479	4000	4599	6399
	STI	107	117	120	118	200	237
15	<u>Static Aged at 185°F for 16 hours</u>						
	Separation, in	None	None	None	None	0.25	0.25
	Settling	None	None	None	None	None	None
	1022 sec ⁻¹ , cp	25	24.5	32.5	27	22	21.5
	511 sec ⁻¹ , cp	31	30	44	35	28	30
20	1022 sec ⁻¹ , cp	100	50	450	200	250	150
	0.0636 sec ⁻¹ , cp	6000	520	24,595	2100	6019	11,618
	STI	194	17	559	57	215	387

Table 814.6 ppg CaBr₂/ZnBr₂ Fluids8 ppb XI.APS, 0.25 ppb MgO

<u>Hr. Aged @ 185°F</u>		<u>0</u>	<u>16</u>	<u>36</u>	<u>62</u>	<u>72</u>	<u>144</u>	<u>316</u>
5	1022 sec ⁻¹ , cp	26.5	27	28.5	29.5	29.5	28	29.5
	511 sec ⁻¹ , cp	34	35	37	39	39	37	39
	340.7 sec ⁻¹ , cp	39	40.5	43.5	46.5	46.5	45	46.5
	170.3 sec ⁻¹ , cp	51	54	57	63	63	63	63
	10.22 sec ⁻¹ , cp	200	200	200	250	300	250	250
10	5.11 sec ⁻¹ , cp	300	300	300	400	400	400	400
	0.0636 sec ⁻¹ , cp	3997	1240	2100	5599	5919	6079	5059
	STI	118	35	57	144	152	164	130
	Separation	-	None	None	None	None	None	None
	Settling	-	None	None	None	None	None	None

What is claimed is:

1. A clay-free well drilling and servicing fluid comprising an aqueous brine containing at least 1.2 equivalents per liter of a water soluble divalent cation salt, a particulate bridging agent which is insoluble in the aqueous liquid, and a starch derivative wherein the concentration of the starch derivative is sufficient to provide the fluid with the following characteristics: (a) a low shear rate viscosity less than about 10,000 centipoise; (b) a high shear rate viscosity at 511 sec^{-1} in the range from about 15 to about 70 centipoise measured at 120°F ; (c) a fluid loss less than about 10 milliliters as measured at 185°F and 250 psi differential pressure across a 5 micron disk for 30 minutes; and (d) anti-settling characteristics as exhibited upon static aging the fluid for 16 hours at 185°F .
2. The fluid of Claim 1 wherein the starch derivative comprises a pre-gelatinized crosslinked amylopectin starch which has been crosslinked to the extent that the viscosity of a basic aqueous amylopectin starch suspension undergoing crosslinking is within about 25% to about 60% of the maximum viscosity which can be obtained.
3. The fluid of Claim 2 wherein the amylopectin starch is crosslinked with epichlorohydrin.
4. The fluid of Claim 3 wherein the density of the fluid is at least about 10 ppg.

5. The fluid of Claim 3 wherein the water soluble divalent cation salt is selected from the group consisting of the alkaline earth metal halide salts, the zinc halide salts, and mixtures thereof.

6. The fluid of Claim 3 wherein the concentration of the starch derivative is
5 from about 5 ppb to about 12 ppb.

7. The fluid of Claim 3, 4, 5, or 6 additionally containing an additive selected from the group consisting of magnesium oxide, dipotassium hydrogen phosphate, and mixtures thereof, in an amount sufficient to increase the low shear rate viscosity without increasing the high shear rate viscosity above 70 centipoise.

10 8. A process of preparing a clay-free well drilling and servicing fluid, the fluid comprising an aqueous brine containing at least 1.2 equivalents per liter of a water soluble divalent cation salt and a particulate bridging agent which is insoluble in the aqueous liquid, which comprises adding to the fluid a starch derivative in an amount sufficient to provide the fluid with the following characteristics: (a) a low
15 shear rate viscosity less than about 10,000 centipoise; (b) a high shear rate viscosity at 511 sec^{-1} in the range from about 15 to about 70 centipoise measured at 120°F ; (c) a fluid loss less than about 10 milliliters as measured at 185°F and 250 psi differential pressure across a 5 micron disk for 30 minutes; and (d) anti-settling characteristics as exhibited upon static aging the fluid for 16 hours at 185°F .

20 9. The process of Claim 8 wherein the starch derivative comprises a pre-gelatinized crosslinked amylopectin starch which has been crosslinked to the extent that the viscosity of a basic aqueous amylopectin starch suspension undergoing

crosslinking is within about 25% to about 60% of the maximum viscosity which can be obtained.

10. The process of Claim 9 wherein the amylopectin starch is crosslinked with epichlorohydrin.

5 11. The process of Claim 10 wherein the density of the fluid is at least about 10 ppg.

12. The process of Claim 10 wherein the water soluble divalent cation salt is selected from the group consisting of the alkaline earth metal halide salts, the zinc halide salts, and mixtures thereof.

10 13. The process of Claim 10 wherein the concentration of the starch derivative is from about 5 ppb to about 12 ppb.

14. The process of Claim 10, 11, 12, or 13 additionally containing an additive selected from the group consisting of magnesium oxide, dipotassium hydrogen phosphate, and mixtures thereof, in an amount sufficient to increase the low shear
15 rate viscosity without increasing the high shear rate viscosity above 70 centipoise.

15. A process of drilling a well wherein a drilling fluid is circulated within the wellbore being drilled as drilling proceeds which comprises using as the drilling fluid the fluid of Claim 1, 2, 3, 4, 5, or 6.

16. In a process of completing or working over a well wherein a subterranean
20 formation is contacted with an aqueous liquid, the improvement comprising using as the aqueous fluid the fluid of Claim 1, 2, 3, 4, 5, or 6.

17. A process of drilling a well wherein a drilling fluid is circulated within the wellbore being drilled as drilling proceeds which comprises using as the drilling fluid the fluid of Claim 1, 2, 3, 4, 5, or 6, wherein the fluid additionally contains an additive selected from the group consisting of magnesium oxide, dipotassium
5 hydrogen phosphate, and mixtures thereof, in an amount sufficient to increase the low shear rate viscosity without increasing the high shear rate viscosity above 70 centipoise.

18. In a process of completing or working over a well wherein a subterranean formation is contacted with an aqueous liquid, the improvement comprising using
10 as the aqueous fluid the fluid of Claim 1, 2, 3, 4, 5, or 6, wherein the fluid additionally contains an additive selected from the group consisting of magnesium oxide, dipotassium hydrogen phosphate, and mixtures thereof, in an amount sufficient to increase the low shear rate viscosity without increasing the high shear rate viscosity above 70 centipoise.

15

INTERNATIONAL SEARCH REPORT

International application No

PCT/US00/20933

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) C09K 7/02

US CL 507/111, 140, 145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. 507/111, 140, 145

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5,641,728 A (DOBSON JR. et al) 24 June 1997, see column 7, line 52 - column 8, line 15 and example 1.	1-18
X	US 5,616,541 A (DOBSON JR et al) 01 APRIL 1997, see examples.	1, 8, 15-18
-----		-----
Y		2-7, 9-14
X	US 5,728,654 A (DOBSON JR et al) 17 MARCH 1998, see examples.	1, 8, 15-18
-----		-----
Y		2-7, 9-14
X	US 5,783,527 A (DOBSON JR et al) 21 JULY 1998, see column 6, lines 1-34.	1, 8, 15-18
-----		-----
Y		2-7, 9-14

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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* O* document referring to an oral disclosure, use, exhibition or other means	
* P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 AUGUST 2000

Date of mailing of the international search report

18 SEP 2000

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/20933

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	US 5,804,535 A (DOBSON JR et al) 08 SEPTEMBER 1998, see claims.	1-18